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A CARBON MONOXIDE RECORDER AND ALARM

BY

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H. W. FREVERT and J. J. BLOOMFIELD

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A CARBON MONOXIDE RECORDER AND ALARM

By S. H. Katz[1], D. A. Reynolds, H. W. Frevert, and J. J. Bloomfield

INTRODUCTION

In the course of its investigations relating to the gases that may endanger the health and safety of workers in mines and industrial plants, the Bureau of Mines has given particular attention to that deadly gas carbon monoxide (CO), which is produced by the incomplete combustion of coal and other fuels. The bureau has studied the physiological effects of the gas, the treatment of persons overcome by it, and the methods of detecting it. At the request of the New York State Bridge and Tunnel Commission, which desired information on the contamination of tunnel air by carbon monoxide in the exhaust gases of automobile engines, the Bureau of Mines made tests to obtain necessary data for a ventilating system for the Holland vehicular tunnels under the Hudson River at New York City now being constructed. The data obtained for the Holland tunnels were applicable to the Liberty vehicular tunnels at Pittsburgh, Pa., completed in 1924. The Liberty tunnels are twin tunnels 5,888 feet long. Midway in each tunnel a two-compartment shaft leads to the fan house at the surface. In the fan house are 8 Sirocco-type fans, 4 of which exhaust the air longitudinally through half of the tunnels while 4 blow air through the other half.

Four parts of carbon monoxide in 10,000 parts of air was determined as the maximum concentration to which a person may be exposed for one hour without noticeable effects; or, if the concentration is increased from zero uniformly for one hour, the maximum concentration tolerable is 6 parts per 10,000, averaging 3 parts per hour.[2] An apparatus that would automatically determine and record such low concentrations of carbon monoxide was obviously desirable and was considered at a conference between C. M. Holland, chief engineer of the Holland tunnel, members of his staff, and members of the Bureau of Mines. Then the Bureau of Mines, through its

[1] This paper submitted to the faculty of the University of Pittsburgh as part requirement for the degree of doctor of philosophy.

[2] Henderson, Yandell, Haggard, H. W., Teague, M. W., Prince, O. L., and Wonderlich, R. M., "Physiological effects of automobile exhaust gas and standards of ventilation for brief exposures," Jour. Ind. Hyg., vol. 3, August, 1921, pp. 72-92 and 137-146.

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Pittsburgh experiment station, undertook the development of a suitable recorder.

The principle employed is measurement by means of thermocouples of the increased temperature of the gases when the CO and oxygen react chemically in the presence of a catalyst, the thermoelectric effects being recorded by means of a recording potentiometer. After extended experimentation and development a recorder was produced which is not appreciably affected by the presence of other gases and which is capable of indicating and continuously recording the highly diluted CO. Operation over a period of six months proved it to be reliable.

Another apparatus gave continuous and satisfactory service for five months at the Liberty tunnels analyzing exhaust air from one section and was still working in January, 1925. This apparatus has enabled health officials to ascertain that the ventilating machinery has operated properly and that the ventilation has been ample at all times. The recorder is equipped with a bell to warn attendants in the fan house should the CO in its section at any time exceed 4 parts in 10,000. Further, the recorder can effect considerable saving in power at the fan house if the volume of air is reduced when the CO is low.

Carbon monoxide recorders should be useful also for promoting economy in boiler furnaces, blast furnaces, and other metallurgical and chemical equipment, and for investigations pertaining to them. They may be useful wherever CO is an important factor because of hygienic, technical, or economic reasons, or in gaseous processes when CO can be introduced as an inert component. The recorder has proved to be the most sensitive instrument known for determining carbon monoxide.[2a]

ACKNOWLEDGMENTS

This investigation was undertaken at the suggestion of A. C. Fieldner, superintendent and supervising chemist of the Pittsburgh experiment station of the Bureau of Mines. Arrangements for installation of the recorder at the Liberty tunnels were made by A. D. Neeld, consulting engineer for the commissioners of Allegheny County, Pa., for the Liberty tunnels. H. C. Bashioum, professor of industrial chemistry in University of Pittsburgh, was advisor throughout the study. F. L. Bishop, dean of the engineering school of the university, was consulted freely. The following employees at the Pittsburgh experiment station assisted: L. F. Perry, W. P. Yant, J. A. Rowe, P. A. Collins, and F. C. Donath.

[2a] After this technical paper was written, some tests with an indicating instrument of nearly the same sensitivity were described by A. B. Lamb and W. E. Vail. "The effect of water and of carbon dioxide on the catalytic oxidations of carbon monoxide and hydrogen by oxygen," Jour. Am. Chem Soc., vol. 47, Jan. 1925, pp. 122–142.

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PREVIOUS DEVELOPMENT OF PRINCIPLES AND INSTRUMENTS

The principle of indicating the presence of combustible gases in air by a differential temperature effect induced by the gases when in contact with a catalyst to promote oxidation dates back many years. In 1889 Pitkin and Niblett [3] devised an instrument consisting of two thermometers in a case pervious to gases; one thermometer was coated about the bulb with platinum black, the other was plain. The thermometers showed the same temperature indications when in pure air, but when combustible gases such as hydrogen or mine gases were present the platinized thermometer indicated a higher temperature than the other, and the concentration of such gases could be estimated from the temperature rise.

Williams and Williams [4] in 1915 patented an instrument using a case pervious to gases, a catalyst, differential thermocouples, and a galvanometer; they combined a signaling device with it. The two opposing junctions of the thermocouple were covered with porous "buttons," one of which was plain and the other impregnated with finely divided platinum or palladium. The buttons were equally heated by means of similar platinum resistances wound about them and were electrically connected in series with a battery. The thermoelectric circuit included a galvanometer or millivoltmeter and a relay. In impure air the galvanometer indicated the percentage of the deleterious gas. When enough gas was present, the relay closed a second circuit of greater power, which rang a warning bell.

Chance and Chance [5] obtained a patent in 1919 for a device in which a mercury-filled bulb joined to a tube was surrounded by a catalyst, which in turn was surrounded and heated by a liquid bath maintained at boiling. Air was drawn through the catalyst by means of an exhauster or by a chimney effect. The copper oxide catalyst acted on carbon monoxide and hydrogen but did not oxidize methane unless kept at some higher temperatures. The mercury stood at a predetermined height so long as air only was present. When enough CO (or other combustible gas) entered, the mercury rose because of the greater heating and closed an electric circuit, causing a signal to operate.

In 1917 the Bureau of Mines undertook investigations of war gases The work led through numerous ramifications,[6] including the development of hopcalite, a catalyst that causes oxidation of CO in air at

[3] Pitkin, J., and Niblett, J. T., "Improvements in instruments for indicating the presence of hydrogen gases or fire damp in mines or other places," British Patent 4629, 1889.

[4] Williams, A., and Williams, L. D., "Contrivance for automatically detecting the presence of certain gases and vapors," U. S. Patent 1143473, June 15, 1915.

[5] Chance, T. M., and Chance, E. M., "Detecting combustible gases," U. S. Patent 1298890, Apr. 1, 1919.

[6] Manning, Van. H., War Gas Investigations. Bull. 178A, Bureau of Mines, 1919, 37 pp.

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ordinary temperatures.[7] Hopcalite is a specially prepared mixture of manganese dioxide and copper oxide in granular form [8] and was first used in gas-mask canisters for the purpose of destroying CO.[9] Although it was known about 40 years before that some base-metal oxides cause at low temperatures catalytic oxidation of CO in the presence of oxygen,[10] the knowledge was not applied practically until hopcalite was used in gas masks.

While testing the action of CO gas-mask canisters, Lamb and Larsen [11] used a CO tester consisting of a platinum catalyst surrounding one junction of a pair of differential thermocouples. The thermocouples were held in a tube through which a steady stream of the gas passed, and the series of tubes was inclosed in a vapor bath of diphenylamine to maintain a uniform temperature of 325° C. The thermocouple leads connected with a galvanometer that indicated a difference in potential between the thermocouple junctions when CO was present. Deflections of the galvanometer were calibrated against known concentrations of CO in air passed at a uniform rate. Lamb and Larsen [12] also describe hopcalite in a gas detector applied to gas-mask canisters to signal the presence of CO by the closing of an electric circuit through expansion of bimetallic strips from the heat of oxidation of CO, or from the effect of the heat on one junction of a thermocouple in a circuit with a potential indicator; they mention that soda lime and charcoal may precede the hopcalite. Another device for warning of the presence of CO, made with bimetallic strips in presence of a catalyst, was recently tested in South Africa.[13]

Some instruments had been made previously to record relatively high concentrations of CO,[14] but they are quite different in principle from those heretofore described, and so need no further attention here.

---

[7] July 1, 1918, the Bureau of Mines war-gas investigations were transferred to the Chemical Warfare Service, U. S. Army, which had then been recently organized. Since January 1, 1919, the bureau has investigated and developed gas masks for industrial purposes at its Pittsburgh experiment station.

[8] Frazer, J. C. W., and Scalione, C. C., "Catalyst and process for making it," U. S. Patent 1345323, June 29, 1920.

[9] Lamb, A. B., Bray, W. C., and Frazer, J. C. W., "The removal of carbon monoxide from air," Jour. Ind. and Eng. Chem., vol. 12, March, 1920, pp. 213–221. Katz, S. H., Bloomfield, J. J., and Fieldner, A. C., The Universal and Fireman's Gas Masks, Tech. Paper 300, Bureau of Mines, 1923, 22 pp.

[10] Wright, C. R. A., and Luff, A. P., "Researches on some points in chemical dynamics," Jour. Chem. Soc., vol. 33, 1878, pp. 1–27 and 504–545.

[11] Lamb, A. B., and Larsen, A. T., "The rapid determination of carbon monoxide in air," Jour. Am. Chem. Soc., vol. 41, December, 1919, pp. 1908–1921. "Testing gases," U. S. Patent 1321063, Nov. 4, 1919.

[12] Lamb, A. B., and Larsen, A. T., "Gas detector," U. S. Patent 1416361, May 16, 1922.

[13] Vaughn, J. A., "Notes on a carbon monoxide detector and alarm," Jour. South African Inst. Eng., vol. 22, February, 1924, pp. 98–103

[14] Chemical and Metallurgical Engineering, "A new automatic oxygen, carbon monoxide, and carbon dioxide recorder," vol. 15, 1916, pp. 542–544. Rideal, E. K., and Taylor, H. S., "Apparatus for indicating and recording quantities of carbon monoxide in hydrogen and other gases," Canadian Patent 204994, Oct. 26, 1920. Taylor, G. B., and Taylor, H. S., "Automatic volumetric analysis carbon monoxide recorder," Jour Ind. and Eng. Chem., vol. 14, November, 1922, pp. 1008–1010. Engineering and Mining Journal-Press, "Novel recorder will indicate CO content," vol. 116, Dec. 8, 1923, p. 1011. Palmer, P. E., and Weaver, E. R., Thermal Conductivity Method for the Analysis of Gases, U. S. Bureau of Standards Technol. Paper 249, Jan. 7, 1924, 100 pp. Fuels and Furnaces, "At last, a CO meter," vol. 1, October 1923, pp. 471–472.

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Certain devices that were employed for other purposes have been incorporated in the mechanism of the CO recorder to be described. These include the flow meter of Fieldner, designed for use in testing canisters with gases,[15] and the device of Mase [16] for maintaining a constant flow of gases.

Since January 1, 1919, the Bureau of Mines has continued at its Pittsburgh experiment station to develop CO gas masks for use in mines and other industries. Although development of the CO recorder proceeded partly in conjunction with gas-mask studies, the active undertaking was initiated by the need of continuously recording the CO in vehicular tunnels.

DESCRIPTION OF CARBON MONOXIDE RECORDER

PRINCIPLE

When carbon monoxide (CO) unites chemically with oxygen (O_2) to form carbon dioxide (CO_2), according to the equation

$$2\,CO+O_2=2\,CO_2+\text{heat (67,960 gram-calories per gram-molecule of CO)}$$

the heat liberated increases the temperature of the gases themselves and of the matter in contact with them. The recorder uses this effect as a means of indicating as well as recording the concentration of the CO in air. Hopcalite, a catalyst, promotes the union of the CO and O_2. Thermocouples generate electric potentials which increase with the temperature, hence with the CO content, and the effects are recorded by a recording potentiometer. The recording potentiometer includes mechanism to operate electric bells or signals when the CO attains a concentration of 4 parts per 10,000, or it may be set to ring at other predetermined concentrations.

MECHANISM AND STRUCTURE

Plate I shows the CO recorder installed at the fan house of the Liberty tunnels. The parts are all mounted upon a stand composed of a table 24 by 40 by 30 inches high, with a backboard 40 by 48 inches attached. The top of the backboard stands 6½ feet above the floor. The table has a shelf 24 by 40 inches, 6 inches above the floor; a drawer is included under the table top.

Figure 1 shows the essential parts of the apparatus. Arrows indicate the course of the gas from left to right. The gas is drawn through pipes leading from the air ducts of the exhaust fans to a motor-driven blower, *a*, which forces it through the remaining appara-

[15] Fieldner, A. C., "Methods and apparatus for testing canisters," U. S. Patent 1307813, June 24, 1919.

[16] Mase, R. P., "Constant-flow gas regulator," U. S. Patent 1494856, May 20, 1924. Oberfell, G. G., and Mase, R. P., "An automatic compensating flow meter," Jour. Ind. and Eng. Chem., vol. 11, April, 1919 pp. 294-296.

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tus. Tubing connects the parts through which the gases flow. Gas drawn by the pump in excess of requirements is wasted through a side outlet with a hand-regulated globe valve, as shown. The gases pass on through the four bottles b_1, b_2, b_3, b_4 in series; the second and third bottles contain sulphuric acid wash to dry the gases and remove hydrocarbons, ammonia, and other gases soluble in or retained by sulphuric acid; the first and fourth bottles serve as traps to prevent passage of acid to other parts of the apparatus. The gases next pass through a receptacle, *c*, containing a mixture of granular activated charcoal and soda lime or other caustic and filters of absorbent cotton. These allow the air and CO to pass through but retain all other gaseous impurities or suspensoids that may materially affect the catalyst following. Hydrogen (H_2), methane (CH_4), and some carbon dioxide (CO_2), if present, are not restrained, but these gases at their low concentrations do not impair the accuracy of the apparatus, because methane is not oxidized by nor does it affect the catalyst at the temperatures employed. Hydrogen, as will be shown later, has an effect so small that it may be disregarded, and carbon dioxide is practically inert.

In Figure 1, *d* is a water well used to adjust the rate of gas flow, *e* is an orifice-type flow meter with water-filled manometer to indicate the flow, and *f* is a reservoir of water which drains into *d* through tube *g*. An escapement tube, *h*, for gas dips into the well *d*. It allows gas to pass out through an opening, *i*, when the gas pressure in the apparatus equals the hydrostatic pressure. Varying the depth of the escapement tube in the water adjusts the flow of gas through the flow meter. The arrangement of *d*, *e*, and *f* and connections maintains a constant flow of gas, regardless of variations in the resistance of the succeeding parts of the apparatus. This constant flow is accomplished by increasing or decreasing automatically and equivalently the depth of water in well *d* as the pressure in the apparatus increases through any increased resistance to the flow of gas. A constant pressure difference is thereby maintained across the orifice of the flow meter,[17] gas always escaping from the tube *h*, hence the rate of flow remains constant.

The gases pass to the receptacle *j* containing broken, fused calcium chloride ($CaCl_2$) for removing any additional water vapor. From there they pass to the steam bath *k*, which is heated by a gas flame. A reflux condenser, *l*, stops escape of steam and also constitutes a vent which maintains atmospheric pressure in the steam bath. The bath thus provides a temperature as constant as the barometer. The gas passes through coil *m* in the steam bath, where it is heated to steam

[17] Oberfell, G. G., and Mase, R. P., "An automatic compensating flow meter," Jour. Ind. and Eng. Chem., vol. 11, April, 1919, pp. 294–296. Mase, R. P., "Constant-flow gas regulator," U. S. Patent 1494856, May 20, 1924.

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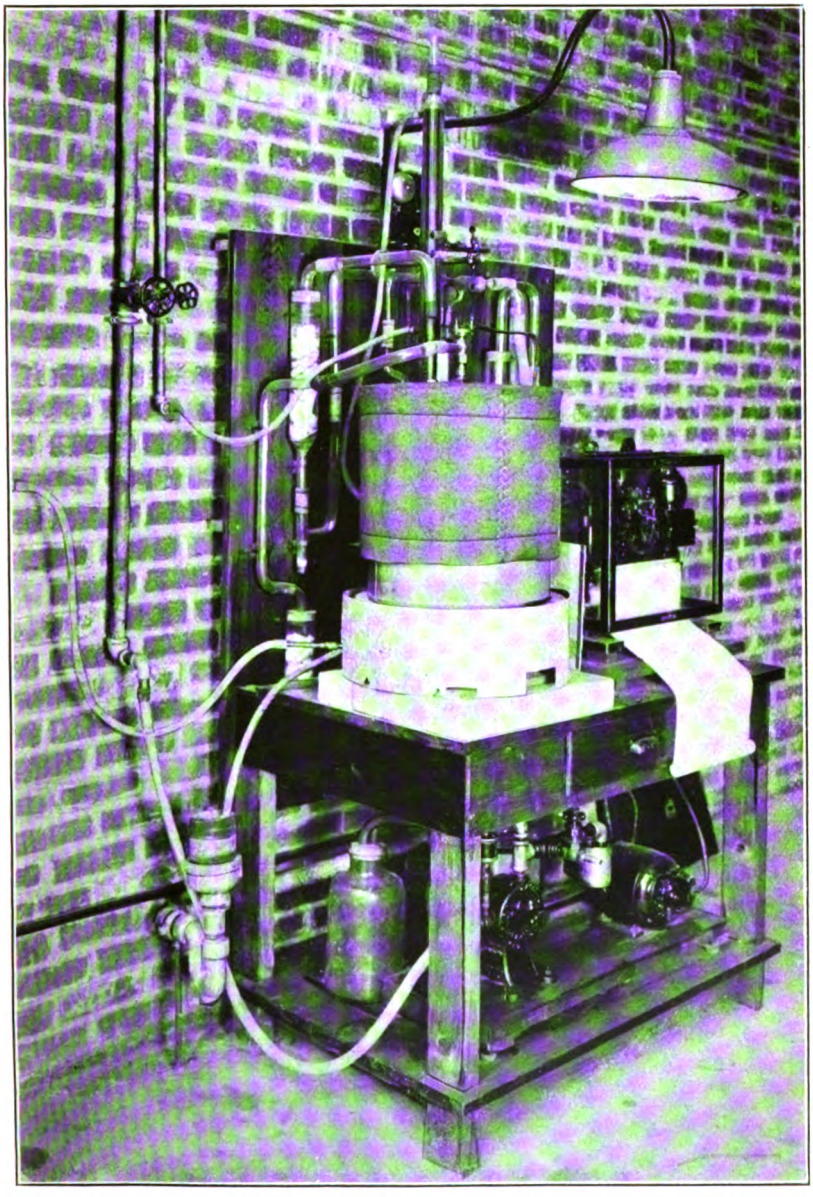

CARBON MONOXIDE RECORDER AT LIBERTY TUNNEL

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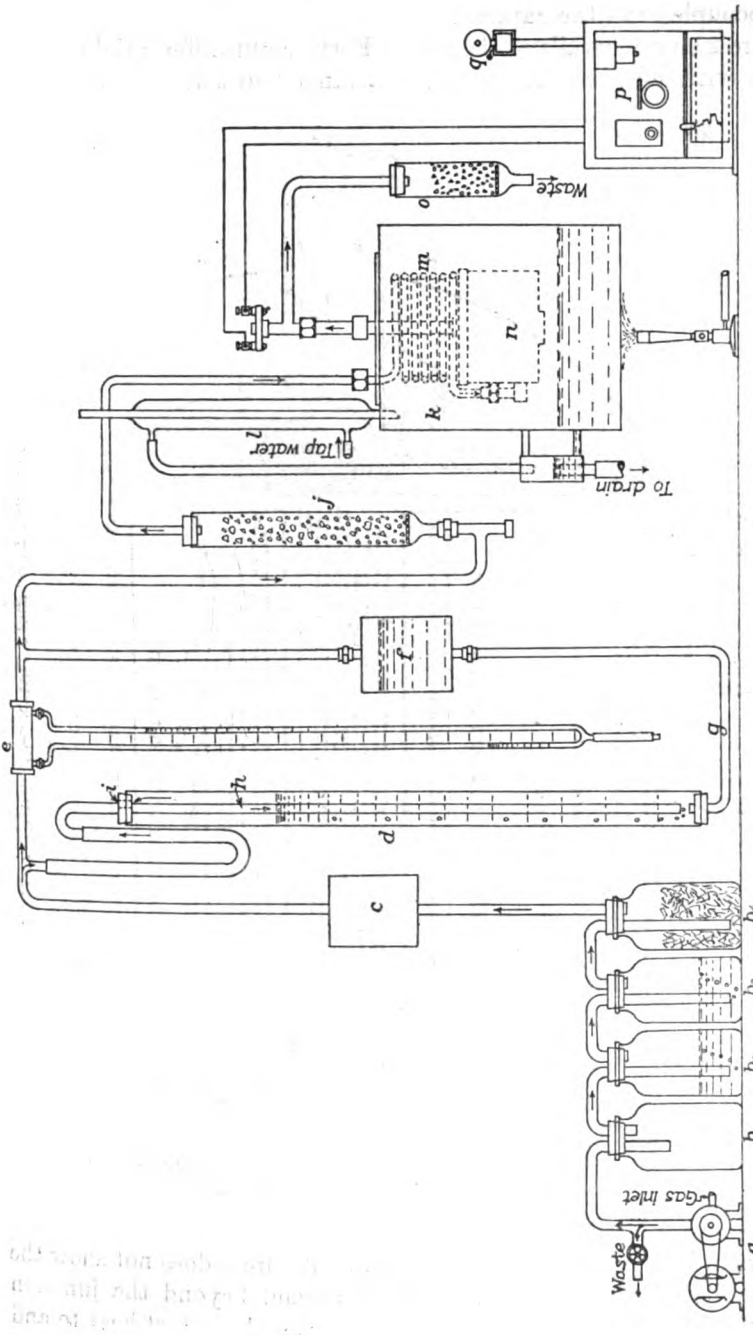

FIGURE 1.—Diagram of essential parts of carbon monoxide recorder. For explanation, see text

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temperature (100° C.), then through the box *n*, which contains the thermocouples and the catalyst.

Figure 2 shows details of the box. Forty-eight differential thermocouples with soldered junctions are arranged in series on two mica

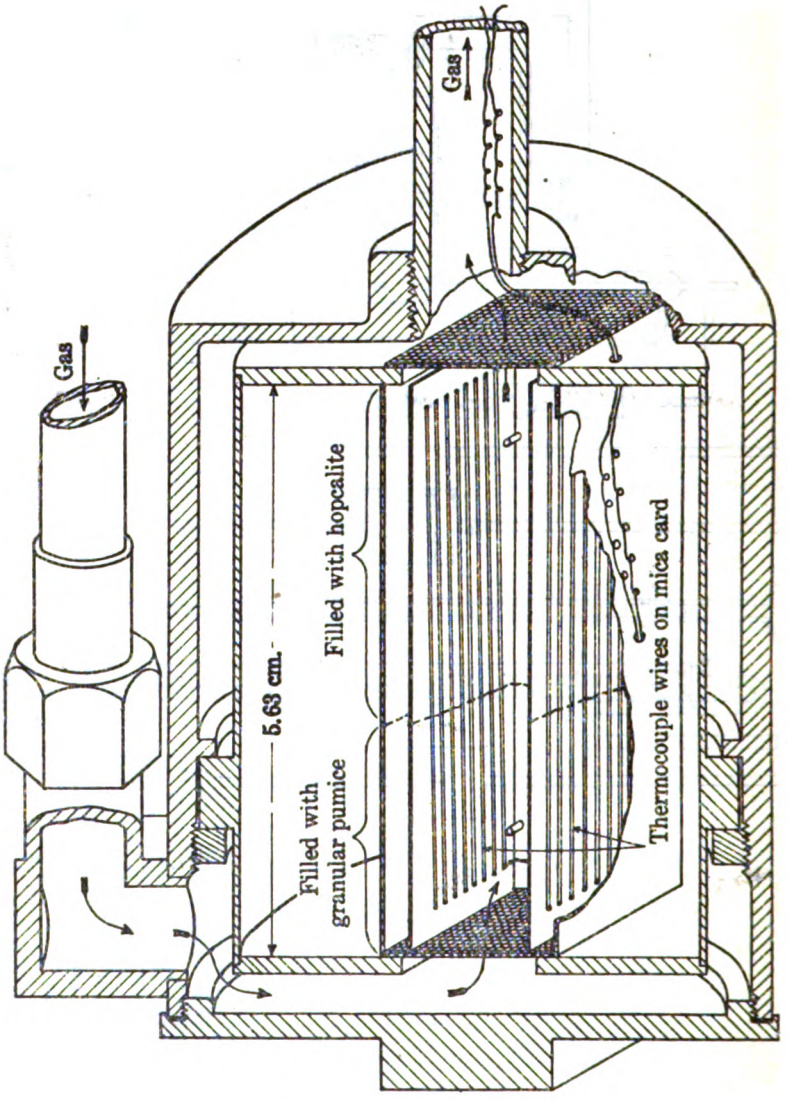

FIGURE 2.—Details of cell containing thermocouples and catalyst

sheets held in a cell mounted in the box. Figure 3 does not show the ends of the thermocouple wires which extend beyond the junction and away from the cards to engage the gases and conduct heat to and from the junctions. The leads from the couples extend to binding posts on top of the steam bath. Granular pumice stone surrounds

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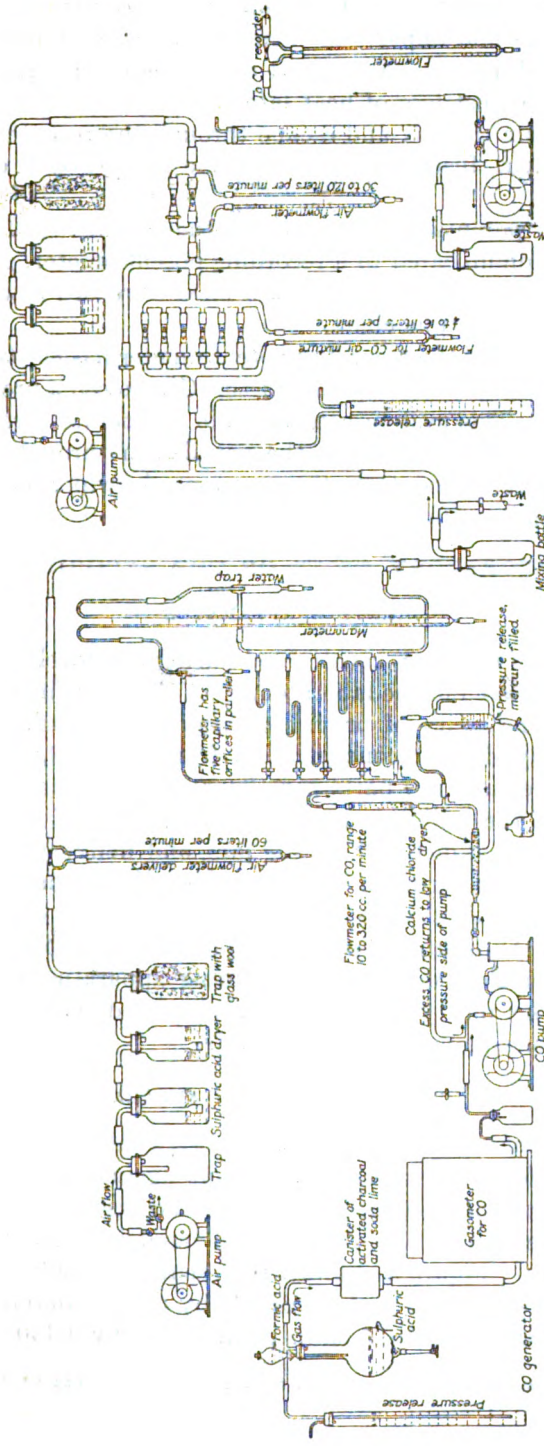

FIGURE 3.—Diluting apparatus for continuously producing carbon monoxide (CO) diluted with air to concentrations between 1 and 5,000 parts per million

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the lower thermojunctions. Granular hopcalite surrounds the upper thermojunctions and imparts to them the increased temperature due to the chemical action. A trapped air space around the cell serves to insulate it against loss of heat laterally. The gases pass through the cell and from the box and escape through the receptacle *o*, which contains broken, fused calcium chloride to prevent entrance of moisture.

The electric potentials impressed on the leads from the thermocouples are communicated to a recording potentiometer, *p*, graduated to indicate CO in parts per 10,000, and fixed to record it with ink in a continuous line on a time chart.

The mechanism of the recording potentiometer has electric contacts to ring the bell *q* as a warning should the CO exceed a predetermined concentration. This system can be made to operate a relay switch, thereby automatically increasing the ventilation through electrically driven fans, or it can control other processes in which CO may be a factor or be made a factor.

LABORATORY TESTS OF THE RECORDER

DILUTING APPARATUS

Many types of recorders constructed during the development of the final type were tested in the laboratory with synthetic mixtures of CO and air. The necessity of providing large volumes of air with CO admixed in any desired concentration from 1 to 10,000 parts per million (latter equals 100 parts per 10,000, or 1 per cent) led to the construction of the "diluting apparatus," a system of gas pumps for air and for CO, flow meters,[18] mixing jars, and delivery tubes, shown diagrammatically in Figure 3. The figure is self explanatory. As the tests of the recorders were based largely on the concentrations obtained with the diluting apparatus, precision of the dilutions was essential. Each flow meter of the diluting apparatus was carefully calibrated. The purity of the CO used was determined and the recording potentiometers were calibrated.

ACCURACY OF DILUTING APPARATUS

Flow meters of the diluting apparatus were calibrated by comparing the heads of water in the manometers against flow rates determined with a gas meter attached in series and discharging into room air, or by determining the volumes delivered into gas burettes in measured times. Figure 4 shows a representative calibration of one of the capillary-tube flow meters for CO by the gas burette method. The capillary was about 0.5 mm. in diameter by 1,130 mm. long.

[18] Benton, A. F., "Gas flow meters for small rates of flow," Jour. Ind. and Eng. Chem., vol. 11, 1919, pp. 623-629.

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The flows through the capillaries are directly proportional to the heads of water or pressure differences, as stated by Poiseuille's law.[19]

Deviations of the determined points from the straight line are due more probably to errors of observation and manipulation than to irregularities in gas flow. The greatest deviation of points from the line in Figure 4 amounts to 3 per cent, but the average deviation of the five points is less than 2 per cent. The latter figure may be taken as the average error of the measurement of the gases by flow meter. Flow meters were used only at water heads exceeding 10 and up to 120 cm.

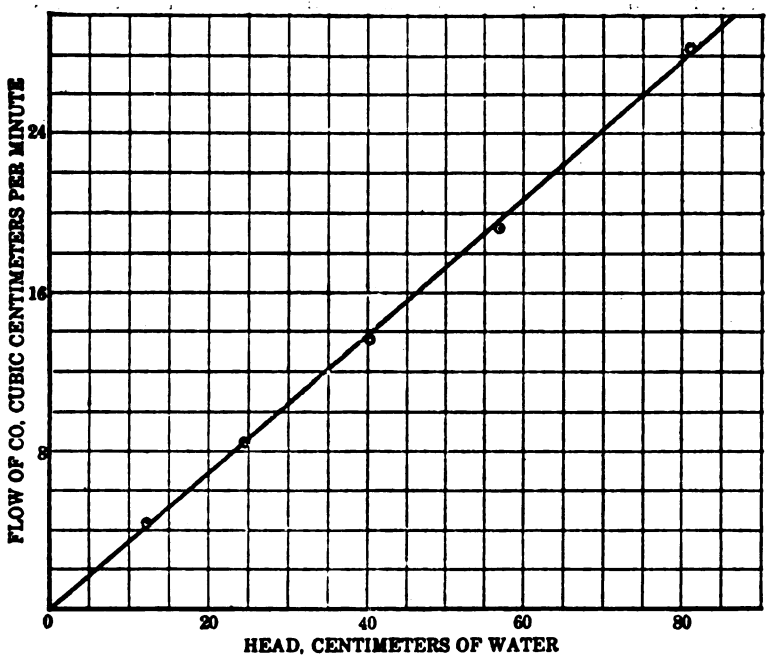

FIGURE 4.—Calibration of a flow meter with glass capillary orifice about 0.5 mm. in diameter by 1.1 meters in length, for delivering carbon monoxide at low rates of flow

The flow meters for measuring the large volumes of air do not give straight-line calibrations, because the flow of air becomes turbulent due to the larger orifices. Figure 5 shows the calibration of a flow meter designed to deliver 60 liters of air per minute. The orifice was a glass tube approximately 5 mm. in diameter by 55 mm. long.

As several flow meters were used concurrently in series or parallel, cumulative errors could increase the inaccuracies beyond the 2 per cent average of the individual flow meters. It is improbable, however, that the total errors of dilutions exceeded an average of 5 or 6 per cent. The dilutions were checked by analyzing samples of the

[19] Poiseuille, J. L. M., "Recherches expérimentales sur le mouvement des liquides dans les tubes de très petites diamètres," Compt. rend. t. 15, 1842, pp. 1167–1196. Washburn, E W., Principles of Physical Chemistry, 2d ed., New York, 1921, pp. 61–63.

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mixtures with the Haldane apparatus, the most accurate gasometric method, and they appeared fully as accurate as the Haldane method, which may vary by 2 parts in 10,000.

PURITY OF THE CARBON MONOXIDE

Carbon monoxide was made by dropping formic acid into heated sulphuric acid. The gas was then passed through a gas-mask canister of activated charcoal and soda lime to remove vapors of formic acid and sulphur dioxide or other vapors and was stored in a laboratory gasometer of 5 cubic feet capacity. A number of samples of gas taken from the gasometers at different times and analyzed by the

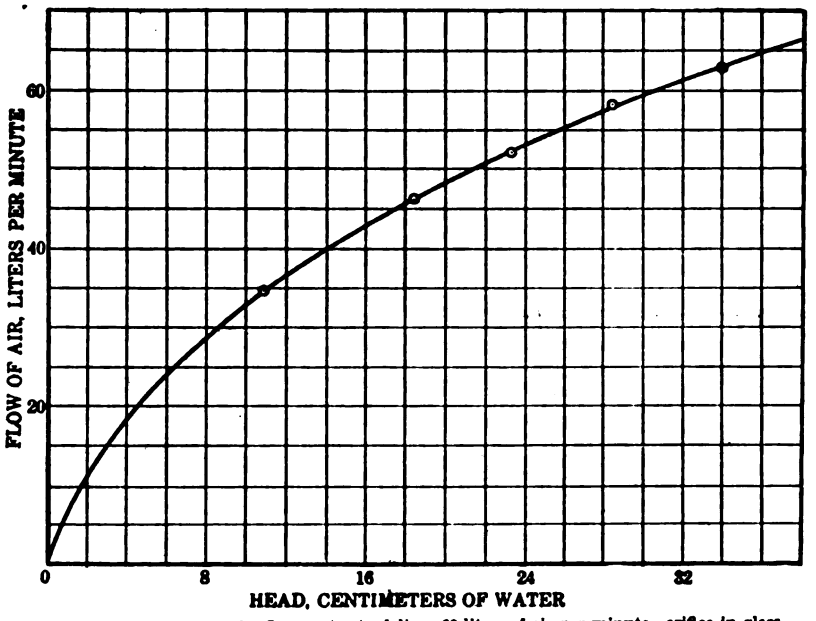

FIGURE 5.—Calibration of a flow meter to deliver 60 liters of air per minute—orifice in glass approximately 5 mm. in diameter and 55 mm. long

combustion method with Orsat apparatus showed 97.8 to 98.5 per cent CO. As the differences only slightly exceeded the errors of analysis, the CO was considered 98 per cent pure, and allowance was made accordingly in computing the calibration of recorders.

CALIBRATION OF RECORDING POTENTIOMETERS

Four Leeds and Northrup recording potentiometers with scale paper 10 inches wide were used. The instruments had ranges across the paper of 3.16, 10, 17.9, and 30 millivolts, respectively. (The instrument with 3.16 millivolts range was made originally with 10 millivolts range, but was modified to increase its deflections.) All the instruments were adjusted to indicate zero potential at a point 1 inch

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from the left edge of the scale, so as to show occurrence of any chance negative potentials as well as the positive potentials due to oxidation of CO.

The deflections of each instrument registered in ink on the scale paper were calibrated against various impressed potentials accurately determined with a standard potentiometric system in the physics laboratory of the Bureau of Mines. Table 1 gives the calibration of the recording potentiometer of 10 millivolts range. The average error of the inked record is 0.06 inch, equivalent to 0.06 millivolt, or less than 1 per cent of the range of the recording potentiometer.

During the earlier tests of the CO recorders the potentials developed by the thermocouples were determined by the recording potentiometers and checked by a Tinsley "vernier potentiometer" and galvanometer, sensitive to 1 microvolt. It was ascertained after usage that the recording instruments were entirely reliable for the purposes, whereupon the Tinsley potentiometer was discontinued.

TABLE 1.—*Calibration of recording potentiometer of 10 millivolts range*

[External resistance less than 1 ohm. Record scale is 10 inches wide and nominally indicates 1 millivolt per inch]

Impressed potential (millivolts)	Deflection of record line from zero (inches)	Deviation from nominal scale (millivolt)	Impressed potential (millivolts)	Deflection of record line from zero (inches)	Deviation from nominal scale (millivolt)
0.902	1.00	+0.10	5.987	5.92	−0.07
2.024	2.00	−.02	7.024	6.96	−.04
3.000	2.96	−.04	8.179	8.07	−.11
4.015	3.97	−.05			
5.014	4.98	−.03	Average		±.06

The recording potentiometers used may be accepted, then, as inherently accurate to 1 per cent of their scale ranges. This degree of accuracy, however, remains only when the external circuits (containing the thermocouples) include total resistances that are comparatively low. On external circuits having a total resistance of 1 ohm or less the recording potentiometers of 10, 17.9, and 30 millivolts ranges repeatedly indicated the same line of potential whether approach was from right or left; the instrument with 3.16 millivolts range approached its line to ±0.05 inch. When 30 ohms was introduced into the latter's circuit, the discrepancy increased to ±0.4 inch, equivalent to 0.125 millivolt or ±4 per cent of the range. External resistance also decreased the speed of response of all the recorders; hence the resistance in circuits of CO recorders should be kept low. If the resistances do not exceed, say, 2 or 3 ohms, the indications of the recording potentiometers may be accepted as

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accurate to 1 per cent, and errors from this source may be considered unimportant.

CHARACTERISTICS OF RECORDERS

EFFECT OF CHANGING RATE OF GAS FLOW

The quantity of heat liberated by oxidation of CO in the catalytic cell depends on the concentration of the CO, the rate at which gas passes through the cell, and the proportion of the CO that is oxidized. Some of the heat is lost by conduction; that remaining increases the temperature of the gases themselves and of the catalyst, thermocouples, and parts of the apparatus in contact with the gas during and after the reaction. If the concentration of the CO is uniform, a

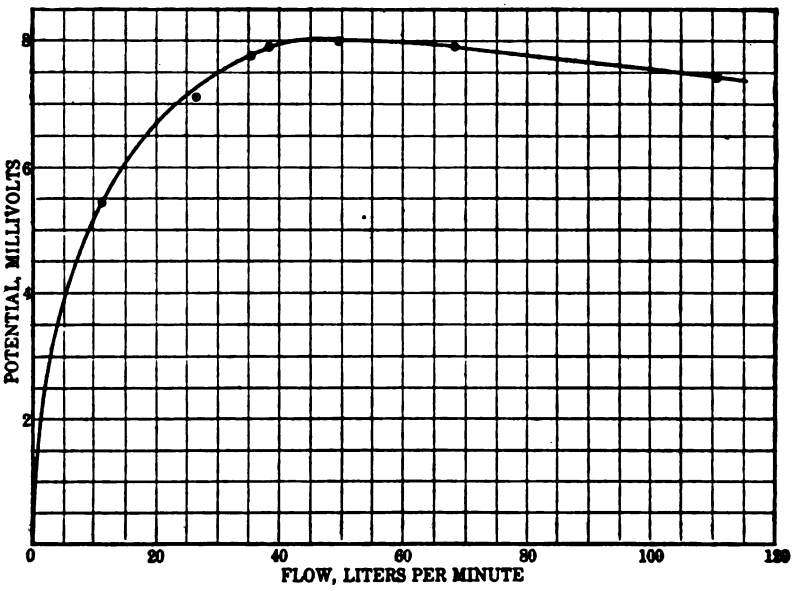

FIGURE 6.—Graph showing effects of increasing rates of gas flow on potentials developed by differential thermocouples with carbon monoxide at 600 parts per million. Cell contained 48 couples in series (volume 100 c. c., depth 5.63 cm.) filled with 60 c. c. of hopcalite above 40 c. c. of granular pumice

condition is reached eventually when no further rise in temperature occurs, then all the heat is dissipated through conduction and through removal in the gas stream. With increasing rates of gas flow up to certain limits the more rapidly the parts are heated to a temperature of equilibrium the more rapid becomes the response of the recorder, and its sensitivity becomes greater. On the other hand, the rate at which the catalyst can bring about the reaction is limited, so that considerable CO gas escapes unburned at excessive rates of flow.

The effects of different rates of gas flow on the potentials developed by the thermocouples are shown in Figure 6. The cell contained 48 differential couples in series (48 silver and 48 constantan wires),

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within a cell volume of 100 c. c., the depth being 5.63 cm. The upper and lower thermojunctions were stationed 4.15 cm. apart and were 0.74 cm. from the top and bottom of the cell. The cell was filled with 60 c. c. of 8 to 20 mesh hopcalite above 40 c. c. of 8 to 20 mesh granular pumice. Carbon monoxide in uniform concentration of 600 parts per million was used for testing. Maximum potential, as shown by Figure 6, developed at a flow of 46 liters per minute. At this point the curve is rather flat, so that minor variations of flow produce only a negligible change in potential; advantage is taken of this in operation. However, the peak becomes increasingly sharp

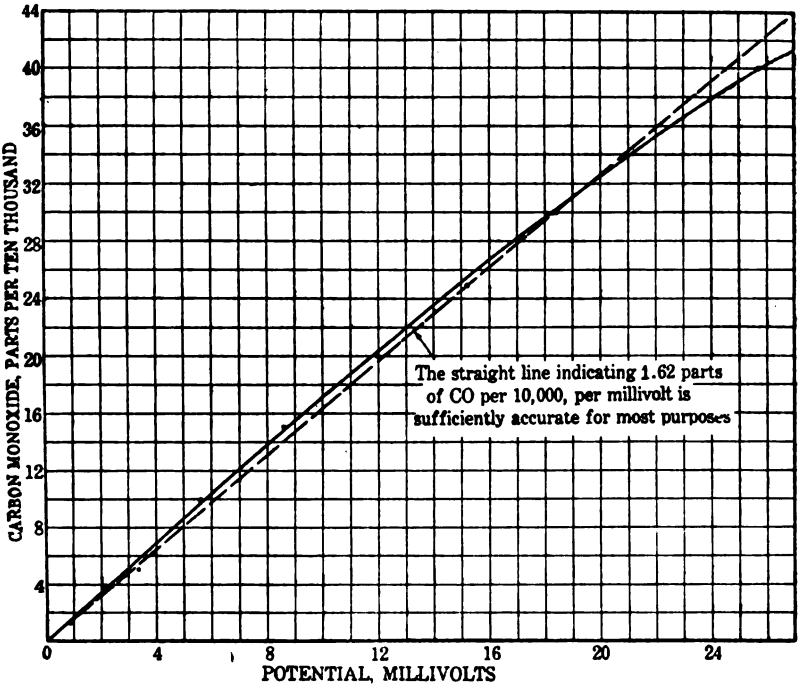

FIGURE 7.—Calibration of cell containing 24 differential thermocouples against carbon monoxide at various dilutions in air and at best rate of flow (33 liters per minute)

in curves of greater concentrations of CO, and vice versa for lower. At rates of flow below 40 liters per minute variations of flow cause relatively large changes in potential; at rates above 50 liters per minute the changes of potential are less pronounced.

Although the thermoelectric effects are greatest at the best rate of flow, considerable CO escapes unburned. A cell of 24 couples was operated at a flow of 33 liters per minute, the best rate, and the outgoing gas was passed through a second apparatus. A practically constant proportion of 15 per cent of the incoming CO escaped when the gas entering the 24-couple cell ranged up to 40 parts per 10,000. The best rate is thus determined by a balance between the amount

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of heat produced, the loss of heat by conduction, and the escape of proportionally more unoxidized CO at the higher rates of flow.

The best rate of flow was determined for each cell before it was calibrated: then calibrations against different concentrations of CO in air were made at the best rate of flow. Figure 7 shows the calibration of the 24-couple cell. The calibration is evidently a slightly curved line. Potential effects greater than the direct ratio show at the higher concentrations, probably because of the more effective oxidation of CO at the higher temperatures.

A similar curvature was found by Lamb and Larsen,[20] who used a platinum catalyst with CO, but they ascribe the curvature to a lesser loss of heat by conduction through oxidation of the CO at higher concentrations within a smaller volume or "reaction zone."

For most practical purposes the straight line, indicated by dashes in the graph, may be accepted as the calibration. It indicates about 0.62 millivolt developed for each part of CO per 10,000, or each millivolt represents 1.62 parts of CO per 10,000 parts of air.

EFFECT OF DEPTH OF HOPCALITE

The effect of varying depths of hopcalite (8 to 14 mesh granules) was determined in a cell having a cross-sectional area of 12.90 square centimeters, and containing 12 differential thermocouples. In this cell the depth and other general arrangements were the same as described for the 48-couple cell. The depth of hopcalite was computed from the cross-sectional area of the cell and from the measurement of the volume of hopcalite in a graduate. The results, presented in Figure 8, show the best depth of hopcalite to be 3.4 cm. above a 2.2-cm. layer of granular pumice, or 60 per cent of the cell depth. This gives a proportion of two-thirds hopcalite and one-third pumice for the space between the thermocouple junctions; and it was used in all further experiments with cells of this depth.

Each point of Figure 8 represents the sensitivity at its respective best rate of flow; these flows were 8.0 liters per minute for the 1.15-cm. depth, 14, 16½, 31, and 45 liters per minute. The speed of response of the recorder to changes in CO concentration was always hastened by increasing the rate of flow. Using the best depth and best rate, the 12-couple cell responded to a change of CO concentration in 20 seconds. The record of the change was 67 per cent completed at 1 minute after the change, 90 per cent at 2 minutes, 95 at 2¾ minutes, and the position of precise indication was attained in 4 to 8 minutes.

Another cell was made 10.8 cm. deep (as compared with 5.63 cm. for previous cells), 18.20 square centimeters cross-sectional area (like the previous 48-couple cell), and containing 48 differential couples of

[20] Lamb, A. B., and Larsen, A. T., "The rapid determination of carbon monoxide in air," Jour. Am. Chem. Soc., vol. 41, December, 1919, pp. 1908–1921.

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No. 18 (B. & S. gauge) constantan wire and No. 21 copper wire. Tests of this cell with varying depths of hopcalite showed the best depth to be 4.7 cm. However, the cell showed no increased thermoelectric effect when used with its best rate (80 liters per minute), so the shallower cells were mostly employed.

EFFECT OF INCREASING THE NUMBER OF THERMOCOUPLES

A set of cells was made with thermocouples in series of 6, 12, 24, 48, and 96. All cells were the same depth, 5.63 cm. The cross sections were increased as the number of thermocouples required, and ranged between 2.54 by 2.54 cm. for the 6 couples to 4.60 by

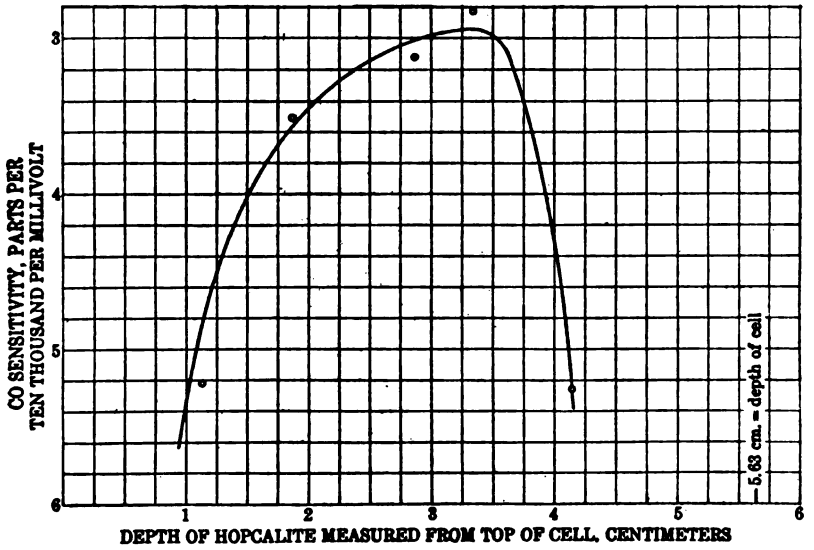

FIGURE 8.—Effect of various depths of hopcalite on sensitivity of cell containing 12 differential thermocouples. Granular pumice was used to fill cell space that remained after adding hopcalite

7.14 cm. for the 96 couples. The 6, 12, and 24 couple units were mounted on single mica cards, the 48 on two cards, and the 96 on three cards. All of these couples were made of silver and constantan wire, respectively, No. 28 and 18 (B. & S. gauge). Copper wire in place of silver was tried in other cells and seems to be nearly as good, the cells developing almost equal potentials and having nearly equivalent resistances.

The principal characteristics of the series of cells are listed in Table 2. Resistances ranged from 0.274 ohm for the 6 couples to 3.78 ohms for 96 couples. The 6, 12, 24, and 48 couple cells developed potentials nearly proportional to the respective numbers of couples, showing about 0.27 millivolt per couple for each part of CO per 10,000. This agreement is excellent. The 96 couples gave

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about 0.25 millivolt per couple. The decrease is not an unusual deviation, as later figures (p. 20) will show, and is due probably to irregularities in the flow of gas or to channeling through various parts of the cross section because of irregularities in the interlocking of the granules. The best rates of gas flow based on the square centimeter unit of cross section also increased with the cross-sectional area of the cell, ranging from 1.71 to 2.74 liters per minute. Reasons for this increase are obscure, unless channeling is a contributing cause.

TABLE 2.—*Characteristics of cells containing different numbers of thermocouples*

[Depth of cells, 5.63 cm.; thermocouples, No. 28 silver and No. 18 constantan (B. & S. gauge) wires. Thermojunctions were soldered and hot and cold junctions were set, respectively, 0.74 cm. from top and bottom of cell, spacing junctions 4.15 cm. apart. Hopcalite layers, 8 to 14 mesh granules, at top of cells were 3.4 cm. deep, which includes two-thirds of distance between thermojunctions. Each couple develops 0.0433 millivolt per degree centigrade between 100 and 190°]

Number of differential thermocouples	Resistance of couples and leads (ohms)	Cross-sectional area of cell (square centimeter)	Best rate of gas flow (liters per minute)		Potential developed by 1 part CO per 10,000 parts air at best flow rate (millivolts)	
			Per cell	Per square centimeter	Per cell	Per couple
6	0.274	6.45	11	1.71	0.160	0.0267
12	.492	12.90	29	2.25	.325	.0271
24	.985	14.52	33	2.27	.660	.0275
48	1.97	18.20	46	2.53	1.30	.0271
96	3.78	32.90	90	2.74	2.39	.0249

MAXIMUM THERMOELECTRIC EFFECT OF OXIDIZING CARBON MONOXIDE IN AIR

The highest average potential increase attained by oxidizing CO in increments of 1 part per 10,000 parts of air mixture was found at 0.0297 millivolt per thermocouple in the 12-couple cell. (See highest point of fig. 8.) The figure 0.0275 millivolt per couple for each part of CO per 10,000 (see Table 2) may be taken as an average. It is only 66 per cent of the possible potential according to calculations based on the following data:

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Data used in calculations

Item	Value	Authority
Heat of combustion of CO to CO_2 gram-calories per gram-molecule	67,960	Thomsen.[1]
Weight of 1 liter of air at 0° C., 760 mm	1.2928	Guye.[2]
Specific heat of air at 100° C. and constant pressure calories per gram	0.2430	Swann.[3]
Specific heat of CO_2 at 100° C. and constant pressure ...do	0.2214	Do.
Molecular weight of CO	28.00	Do.
Molecular weight of CO_2	44.00	Do.
Factor for converting CO expressed as parts per million of gas volume (25° C., 760 mm. pressure) into milligrams per liter.	0.001145	Fieldner, Katz, and Kinney.[4]
Factor for converting CO_2 as parts per million of gas volume (25° C., 760 mm. pressure) into milligrams per liter.	0.001800	Do.

[1] Thomsen, J., "Thermochemistry," Longman's Green & Co., New York, N. Y., 1908, p. 232.
[2] Guye, P. A., "Sur les variations de la densité de l'air et la loi de Loomis-Morley," Jour. Chim. Phys., vol. 15, 1917, pp. 561–76.
[3] Swann, W. F. G., "On the specific heats of air and carbon dioxide at atmospheric pressure by the continuous electric method at 20 and 100° C.," Trans. Roy. Soc., vol. 210, 1911, pp. 199–238.
[4] Fieldner, A. C., Katz, S. H., and Kinney, S. P., "Conversion table for gases—parts per million versus milligrams per liter," appendix in Gas Masks for Gases Met in Fighting Fires, Tech. Paper 248, Bureau of mines, 1921, 61 pp.

The calculations are based on unit volume of 1 liter of air and CO mixture at 25° C. and 760 mm. pressure, the CO being 1 part per 10,000 (=100 parts per million by volume), and assuming perfect gases:

$1.2928 \times \frac{273}{298} = 1.1843$ = weight of 1 liter of air at 25° C. and 760 mm. pressure.

$0.001145 \times 100 = 0.1145$ milligram CO per liter = 100 p. p. m.
$= 0.0001145$ gram CO per liter = 100 p. p. m.

$67,960 \div 28 = 2,427$ gram-calories per gram of CO oxidized.

$2,427 \times 0.0001145 = 0.2779$ calorie from 1 part CO per 10,000 per liter (measured at 25° C., 760 mm.).

Mixture of 1 part CO per 10,000 parts produces 1 part $CO_2 + 9,998.5$ parts residual air according to the equation $2CO + O_2 = 2CO_2$, or approximately 1 part $CO_2 + 9,999$ parts air.

$0.001800 \times 100 = 0.1800$ milligram CO_2 per liter.
$= 0.0001800$ gram CO_2 per liter.

$0.0001800 \times 0.2214 = 0.00004$ calorie per ° C. for the CO_2.

$1.1843 \times 0.2430 \times \frac{9,999}{10,000} = 0.28776$ calorie per ° C. for the air.

Total = 0.2878 calorie required to raise the gaseous products of reaction and air from 100 to 101° C.

$0.2779 \div 0.2878 = 0.9656$° C. theoretically possible temperature increase due to oxidation at 100° C. of 1 part CO per 10,000 of air.

One couple was found to develop an average of 0.0275 millivolt due to 1 part CO per 10,000 and the couples gave a potential of 0.0433 millivolt per degree centigrade, therefore—

$0.0433 \times 0.9656 = 0.0418$ mv. from 1 part CO per 10,000, theoretically possible.

$0.0275 \div 0.0418 \times 100 = 65.8$ per cent of the theoretically possible potential was on the average attained by the cells.

And the thermocouples indicate—

$0.0275 \times 0.0433 = 0.635$° C. average rise in temperature of gases due to 1 part of CO per 10,000 parts.

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The maximum efficiency attained in any experiment was 70.5 per cent, indicating a 0.680° C. rise due to 1 part CO per 10,000.

Inability of the cell to indicate a higher temperature difference between the hot and cold junctions of the thermocouples may be due to conduction of heat along the wires or adjacent parts of the cell from the reaction zone to the cold junctions. The cells are insulated laterally by an air space. That no considerable amount of heat passed laterally from the cell was proved by surrounding the cell with an insulation of 85 per cent magnesia. This insulation did not increase the potentials.

REPRODUCIBILITY OF CELLS

The 48-couple cell was refilled four times with hopcalite and pumice in the ratio 60:40, and recalibrated each time. The best flow and the calibration factors were found as shown in Table 3.

TABLE 3.—*Results of calibrations of cell with 48 couples refilled four times*

Filling of cell	Best rate of flow (liters per minute)	Concentration of CO producing 1 millivolt potential taken from calibration graph (parts per 10,000)	Potential produced in 48 differential couples by 1 part of CO in 10,000 (millivolts)
1	42	0.83	1.21
2	43	.80	1.25
3	44	.77	1.30
4	46	.91	1.10
Average	44	.83	1.21

The maximum CO deviation from the average is less than 10 per cent. This indicates that with ordinary care in proportionating the hopcalite and pumice cells may be refilled repeatedly, and if used with an average calibration of 1.21 millivolts per 48 couples (0.025 millivolt per couple) for 1 part CO per 10,000, the error should not exceed 10 per cent of the indicated CO. It is best, however, to recalibrate for each cell filling, which will reduce the relative errors to about 5 per cent or less.

DETERIORATION OF HOPCALITE

The thermoelectric cells heretofore were used only for short periods of testing. However, a hopcalite and thermometer arrangement for indicating CO, shown in Figure 9, was employed as a guide through an extended series of tests. No exact record was kept of the total time the indicator was used, but it amounted to 3 to 7 hours on occasional days when tests were conducted, over a period of months. The instrument was recalibrated several times during this period.

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THERMOMETER AND HOPCALITE INDICATOR FOR CO

The indicator consists, essentially, of a thermometer with the bulb inserted into a layer of hopcalite held in a tube through which air with admixed CO passes. A steam bath in a glass container, heated by a flame, surrounds the tube. A reflux condenser is attached, and a second thermometer has its bulb in the steam bath to indicate any temperature changes due to the barometric pressure. The air flow was measured through a flow meter, then passed through a glass coil preheater before going to the hopcalite. To prevent entrance of water vapor, a guard tube of calcium chloride was interposed in the gas stream before the hopcalite and another after it. The writers first saw this type of apparatus constructed by R. P. Mase.

Gas was passed at the rate of 4 liters per minute, but later it was found that 7¼ liters per minute was the best rate. Calibrations at intervals showed a decrease in sensitivity through deterioration of the hopcalite, as follows:

TABLE 4.—*Decrease in sensitivity of CO indicator used with unpurified room air containing CO*

Date calibrated, 1923	CO per °C. rise of thermometer (parts per 10,000)	Sensitivity, °C. per 1 part CO per 10,000
Apr. 9	1.38	0.72
May 11	2.15	.47
July 31	3.50	.29
Sept. 8	3.73	.27
Sept. 28	4.00	.25

The sensitivity decreased from 0.72° C. for each part CO per 10,000 to 0.25°, or two-thirds in 5½ months. Deterioration of hopcalite is undoubtedly due to the action of impurities in the air which it absorbs or catches, such as oil vapors or droplets from the air pumps, dust and smoke particles, ammonia, and acid gases such as sulphur dioxide. It was found that a gas purifier of sulphuric acid, soda lime, activated charcoal, absorbent cotton filters, and calcium chloride removed the deleterious components without perceptibly affecting the passage of the carbon monoxide.

EFFECT OF MOISTURE

That moisture inhibits the action of hopcalite is well known.[21] The effect on the accuracy of the recorder was found by passing alternately moistened and dry air with CO through a cell that had

[21] Lamb, A. B., Bray, W. C., and Frazer, J. C. W., "The removal of carbon monoxide from air," Jour. Ind. and Eng. Chem., vol. 12, March, 1920, pp. 215-221. Katz, S. H., Bloomfield, J. J., and Fieldner, A. C., The Universal and the Fireman's Gas Masks, Tech. Paper 300, Bureau of Mines, 1923, 22 pp.

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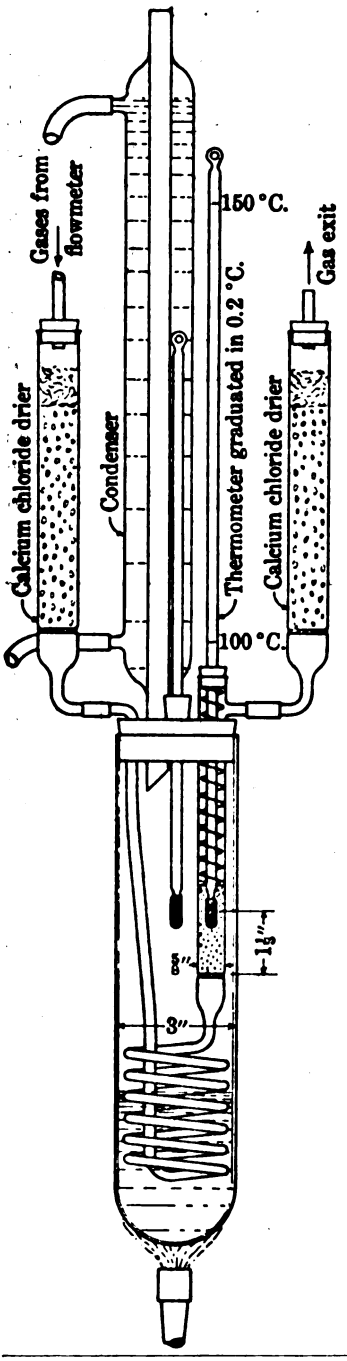

FIGURE 9.—A carbon monoxide indicator with hopcalite and thermometer

first been calibrated with dry gases. The water vapor was kept at a uniform tension of 15.8 mm. of mercury, equivalent to 91 per cent relative humidity at 20° C., and constituting about 2 per cent by volume of the resultant humid gas. Figure 10 shows the effects of the water vapor upon the cell of 24 couples. The potentials were lowered about 14 per cent. In these tests the gases entered the cell at the temperature of saturated steam. At lower temperatures the effect of water vapor on hopcalite is accentuated. Tests showed that the cell recovered fully its original (dry gas) sensitivity in one or two minutes when the moist gas was followed by dry gas. Gases passing into the recorder should, for accurate analysis, be free of moisture.

EFFECT OF HYDROGEN

The gas-purifying system of sulphuric acid, activated charcoal, caustic, absorbent cotton filters, and calcium chloride removes all gases or vapors that can impair the hopcalite or vitiate the CO records, with the possible exception of hydrogen. The action of hydrogen was, therefore, investigated. A statement had been made previously that dry hydrogen (90 per cent) mixed with air (10 per cent) and passed through hopcalite at room temperature showed "no considerable oxidation of hydrogen," but when "the temperature of the affluent gases was raised to about 60 or 70° rapid oxidation of the hydrogen set in."[22]

[22] Lamb, A. B., Scalione, C. C., and Edgar, G., "The preferential catalytic combustion of carbon monoxide in hydrogen," Jour. Am. Chem. Soc., vol. 44, April, 1922, pp. 738–757.

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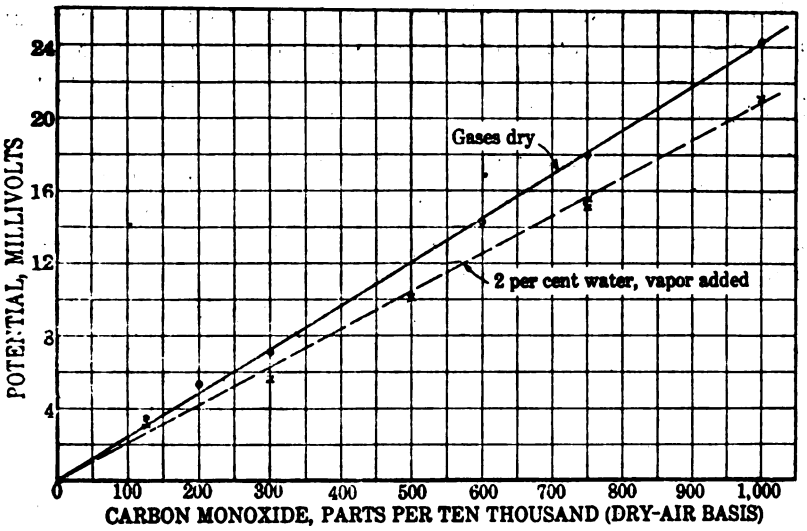

FIGURE 10.—Graph showing lowered potentials developed by the 24-couple cells when the gases are moistened with water vapor at 15.8 mm. pressure (about 2 per cent by volume)

HYDROGEN ALONE IN AIR

Figure 11 shows the potentials developed by the 96-couple cell when dry air containing hydrogen at a dilution of 30 parts per 10,000 was passed through it at various rates of flow, also when CO at 10 parts per 10,000 was passed through. The hydrogen developed a maximum potential of 18.4 millivolts at 15 liters per minute flow, whereas the CO developed a maximum of 24.1 millivolts at about 85 liters per minute flow. At 85 liters flow the hydrogen gave only 5.5 millivolts, or about 0.183 millivolt per 1 part per 10,000. Thus, the effect due to hydrogen alone in air is only about 7.6 per cent of that of the equal partial volume of CO when both are passed at the best flow rate for the carbon monoxide.

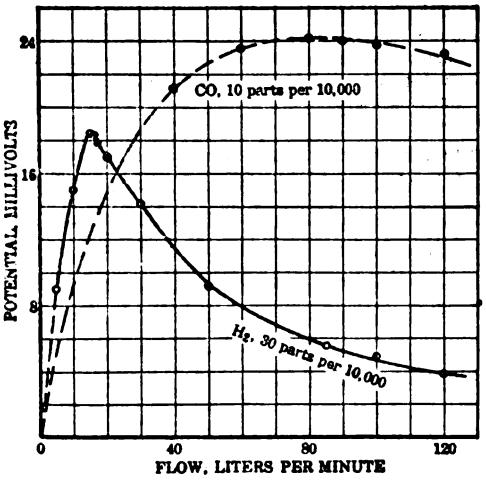

FIGURE 11.—Potentials developed by 96-couple cell with various flow rates of dry air containing 30 parts per 10,000 of hydrogen, or 10 parts per 10,000 of carbon monoxide

Calibration of the 96-couple cell with various concentrations of hydrogen in air up to 50 parts per 10,000 at 85 liters per minute flow (best rate for CO) showed potentials increasing nearly uniformly

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with concentration. A similar calibration at 15 liters per minute (best rate for H_2) gave nearly uniform potential increases up to concentrations of 20 parts of H_2 per 10,000, after which proportionally higher potentials appeared.

HYDROGEN AND CARBON MONOXIDE IN AIR

When mixtures of H_2, CO, and air were passed through the cell of 24 couples, potentials were developed as indicated in Figure 12. This figure shows that a given concentration of H_2 causes a greater increase in potentials when the CO concentration is high than when it is low. The increase must be due to the effect of increased temperature generated by the CO, causing more oxidation of hydrogen. Carbon monoxide and hydrogen are evolved with automobile exhaust gas in the average volume ratio[22] of 1:0.4. The potentials generated in the 24-couple cell by air containing various quantities of CO and H_2 in 1: 0.4 ratio (2.5 volumes CO to 1 volume H_2) were taken from Figure 12 and are shown in Figure 13, together with the calibration in absence of hydrogen. This was done graphically by drawing equipotential lines, as indicated by points taken from Figure 12, on coordinates with concentrations of CO as abscissas and concentrations of H_2 as ordinates, drawing thereon the line indicating CO and H_2 in 1: 0.4 ratio, and taking from the graph the concentrations of CO and H_2 in ratio 1: 0.4 that intersect the various potential lines. Curves similar to Figure 13 were drawn for CO-H_2 mixtures in other ratios, and errors of CO analysis due to the presence of H_2 were taken from them. The results are assembled in Table 5.

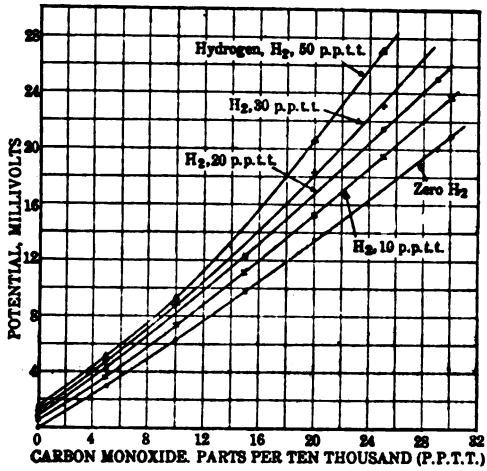

FIGURE 12.—Potentials developed by 24-couple cell with mixtures of carbon monoxide and hydrogen in air, passing at rate of 33 liters per minute (best rate for carbon and monoxide)

[22] Jones, G. W., and Fieldner, A. C., Gasoline Saved on Government Trucks by Adjusting Carburetors by Exhaust Gas Analysis. Reports of Investigations Serial 2487, Bureau of Mines, June, 1923, 13 pp.

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TABLE 5.—*Errors of analysis of CO in air due to presence of H_2 in different proportions*

CO present (parts per 10,000)	Hydrogen (parts per 10,000)	Errors: Excess CO indicated (parts per 10,000)	Errors: Percentage based on actual CO
RATIO OF CO:H_2=1:0.1 BY VOLUME			
1	0.1	0.014	1.4
2	.2	.028	1.4
4	.4	.060	1.5
6	.6	.096	1.6
8	.8	.14	1.8
10	1.0	.19	1.9
15	1.5	.35	2.3
20	2.0	.56	2.8
25	2.5	.80	3.2
RATIO 1:0.2			
1	0.2	0.021	2.1
2	.4	.044	2.2
4	.8	.10	2.5
6	1.2	.17	2.8
8	1.6	.25	3.1
10	2.0	.35	3.5
15	3.0	.66	4.4
20	4.0	1.06	5.3
25	5.0	1.58	6.3
RATIO 1:0.4			
1	0.4	0.034	3.4
2	.8	.074	3.7
4	1.6	.18	4.4
6	2.4	.30	5.0
8	3.2	.46	5.7
10	4.0	.64	6.4
15	6.0	1.25	8.3
20	8.0	2.0	10.2
25	10.0	3.1	12.2
RATIO 1:0.6			
1	0.6	0.058	5.8
2	1.2	.12	6.1
4	2.4	.27	6.8
6	3.6	.46	7.6
8	4.8	.33	8.4
10	6.0	.93	9.3
15	9.0	1.8	11.8
20	12.0	2.9	14.4
25	15.0	4.3	17.3
RATIO 1:1.0			
1	1.0	0.09	9.0
2	2.0	.19	9.6
4	4.0	.43	10.7
6	6.0	.71	11.9
8	8.0	1.1	13.2
10	10.0	1.5	14.6
15	15.0	2.7	18.3
20	20.0	4.5	22.3
25	25.0	6.6	26.4
RATIO 1:1.5			
1	1.5	0.13	13.1
2	3.0	.41	13.8
4	6.0	.61	15.3
6	9.0	1.0	16.9
8	12.0	1.5	18.6
10	15.0	2.1	20.5
15	22.5	3.8	25.5
20	30.0	6.2	31.0
25	37.5		
RATIO 1:2.0			
1	2.0	0.18	18.0
2	4.0	.38	18.9
4	8.0	.82	20.6
6	12.0	1.4	22.5
8	16.0	2.0	24.4
10	20.0	2.6	26.3
15	30.0	4.7	31.8
20	40.0	7.8	38.9
25	50.0		

According to Table 5, the errors of CO analysis, due to the presence of hydrogen in the volume ratio of CO: H_2 = 1: 0.4, range from about 3.4 to 5 per cent of the actual CO when the latter is less than 6 parts per 10,000. Such errors may thus occur in analyses of the atmosphere in tunnels. They can be eliminated by calibrating the recorder for CO in presence of H_2 in 1: 0.4 ratio, but as the errors are small and are on the side of safety their elimination is not essential. At higher concentration of the gases in the same ratio the errors are augmented somewhat; in gases of lesser H_2-CO ratio the errors are smaller. Even with hydrogen twice the concentration of the CO, and with high concentrations of 40 parts per 10,000, the error amounts only to about

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39 per cent based on the actual CO. Even this error may not be excessive for determinations in some circumstances if no better determinations are possible.

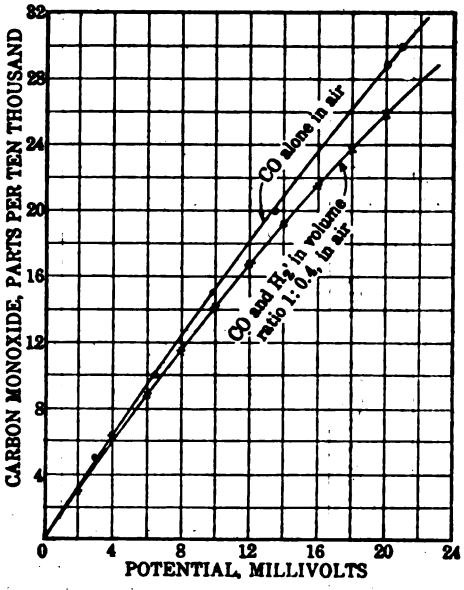

FIGURE 13.—Potentials generated in 24-couple cell by carbon monoxide alone in air, and by air containing carbon monoxide and hydrogen in volume ratio of 1: 0.4; rate of flow, 33 liters per minute (best rate for carbon monoxide)

RECORDER FOR SMALL PROPORTIONS OF CARBON MONOXIDE IN HYDROGEN

A cell kept in an environment of 25° C. was not affected by passage of 50 parts per 10,000 (0.5 per cent) of hydrogen in air, whereas at 25° C. CO in air (passed at its 100° C., best flow rate) exerted an effect on the recorder about one-third as great as at 100° C. The presence of small quantities of CO admixed with relatively large quantities of hydrogen, as for instance in the hydrogen used for producing synthetic ammonia, may thus be recorded by immersing the cell and adjoined gas pipes in a thermostat kept at 25° C. and passing through the cell the gases admixed with a small proportion of air.

RECORDER FOR HYDROGEN

On the other hand, by operating the recorder at 100° C. and at the best rate of flow for hydrogen, it can be made to record small quantities of hydrogen in air. When hydrogen is to be recorded, carbon monoxide should preferably be absent. When both gases are present, however, two instruments may be operated in parallel, one at low temperature and one at high, to record the effects of CC alone and of CO plus H_2. The H_2 can then be estimated by differ-

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ences; or the CO can be determined and eliminated entirely by oxidation at low temperatures, and the residual hydrogen can then be determined in an environment of higher temperatures.

The maximum thermoelectric effect of hydrogen in air was calculated from data on page 23, together with the following:

Additional data used in calculating thermoelectric effect of hydrogen

Item	Value	Authority
Heat of combustion of H_2 to H_2O at 18° C.	68,380 gram-calories per gram	Roth.[1]
Heat of vaporization of water at 100° C. and 1 atmosphere pressure.	538.9 calories per gram	Carlton-Sutton.[2]
Specific heat of steam at 1 kg. per cm.² (99.1° C.—temperature of saturation).	0.486 calorie per gram at 99.1° C., 0.481 at 110° C.	Knoblauch and Raisch.[3]
Specific heat of liquid water	Taken as 1.000 calorie per gram for the temperature range 18° C. to 100° C.	

[1] Roth, W. A., "Die Bildungswarme des Wassers," Zeit. für Electrochem., Jahrg. 26, July, 1920, pp. 288–291.

[2] Carleton-Sutton, T., "A determination of the heat of vaporization of water at 100° C. and one atmosphere pressure in terms of the mean calorie," Proc. Roy. Soc., vol. 93, 1917, pp. 155–176.

[3] Landolt-Bornstein-Roth, Physikalisch-chemische Tabellen, 1923, p. 1276.

The calculation shows 0.813° C. as the maximum theoretical increase in temperature of gases due to oxidation at 100° C. of H_2 in air when at a concentration of 1 part per 10,000.

As compared with this figure, calculations based on the potential measurements and calibration of the thermocouples for temperature effects show an effective temperature rise of only 0.120° C. per 1 part H_2 per 10,000, or 14.8 per cent of the theoretically possible effect. An analysis of the gases escaping from the apparatus when passed at 15 liters per minute showed the following:

Hydrogen entering = 50 parts per 10,000 (by dilution apparatus)
Hydrogen leaving = 43 ± 2 parts per 10,000 (by Haldane analysis)

Thus only 14 per cent of the hydrogen was oxidized.

Another cell operated in a vapor bath at 127° C. increased its potential against hydrogen threefold over that at 100° C.; the best rate remained the same. At this rate potentials due to carbon monoxide increased about 3 per cent. Operating the cell in an environment of higher temperature, 200 or 300° C., would increase the precision of the recorder in determining hydrogen alone in air.

EFFECT OF CARBON DIOXIDE

When carbon dioxide gas (CO_2) is present, some of it may be removed by the soda lime in the canister for purifying the gases, but most of it passes through with the air and CO. Mixtures of CO and air with added CO_2 up to 8 per cent were tried in the recorder with 96 thermocouples and a temperature of 100° C. The increasing CO_2 had a linear decreasing effect on the electric potentials generated by the CO, as compared to equal CO concentrations in the absence of

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CO_2; but the decrease was small, the potentials decreasing only 0.60 per cent for each per cent of CO_2 present.

Calculations based on thermochemical data given on page 19 indicate that the decrease in potential due only to the greater heat capacity of CO_2 per unit volume is 0.48 per cent for 1 per cent of CO_2. The 0.12 per cent difference may be due to mass action of the CO_2 in opposing the oxidation of CO or to CO adsorbed on the hopcalite preventing some of the catalytic action. Lamb and Vail [24] find a similar but much greater effect of adsorbed CO_2 upon the action of hopcalite at 25° C. The very small effects of the CO_2 at 100° C. may be ignored in most practical applications of the CO recorder. If elimination of the effects of the CO_2 should be desirable for some special purpose, a more effective CO_2 absorbent may be included in the gas-purifying train.

PERFORMANCE OF CO RECORDERS DURING EXTENDED USE

CO RECORDS FROM EXHAUST GASES OF A GASOLINE ENGINE

A CO recorder was operated through a period of six months in connection with physiological tests of gasoline-engine exhaust gases. Fresh air diluted the exhausts until the CO concentrations approximated 1 to 4 parts in 10,000. Then the gases were passed through a chamber where the CO was recorded during all test periods lasting about seven hours per working day.

Plate II shows this recorder. All tubes were of glass, connected with rubber nipples, and the parts were assembled on a wooden frame designed to set on a table or bench. The thermocouples were a series of six pairs set lengthwise along a diametrical plane in a glass tube holding pumice and hopcalite. Except for the thermocouple construction in the cell, the glass parts and connections were similar to those of the thermometer-and-hopcalite indicator for carbon monoxide.

The air in the chamber was sometimes sampled, simultaneously with the operation of the recorder, continuously and at a uniform rate to obtain composite samples. Two such samples were taken each day, one in the morning and one in the afternoon. They were analyzed by the blood-pyrotannic acid method, accurate to about one-half part per 10,000.[25] The average concentration of CO was determined from the recorder graph by integrating the time-concentration area and dividing by the time. A statement of the accu-

[24] Lamb, A. B., and Vail, W. E., "The effect of water and of carbon dioxide on the catalytic oxidation of carbon monoxide and hydrogen by oxygen," Jour. Am. Chem. Soc., vol. 47, January, 1925, pp. 122–142.

[25] Sayers, R. R., Yant, W. P., and Jones, G. W., The Pyrotannic Acid Method for the Quantitative Determination of Carbon Monoxide in Blood and Air, Report of Investigations, Serial 2486, Bureau of Mines, June, 1923, 6 pp. Also Tech. Paper 373, Bureau of Mines, 1925, 17 pp.

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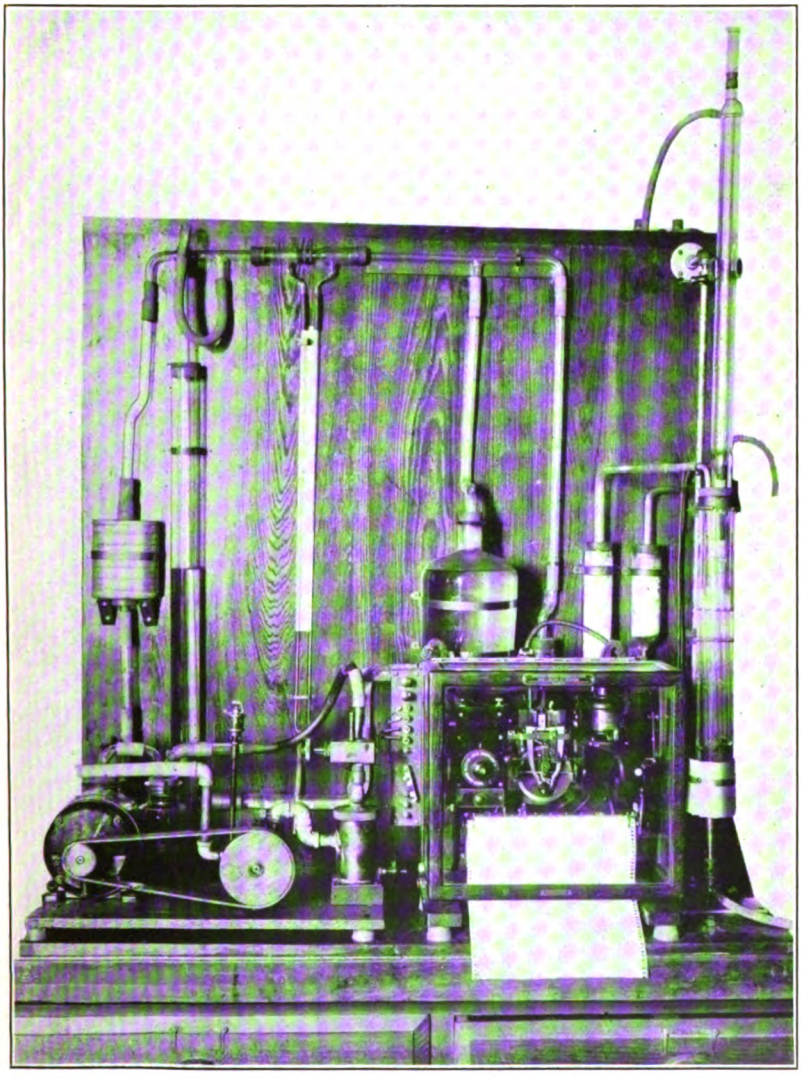

CARBON MONOXIDE RECORDER CONSTRUCTED OF GLASS TUBING

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racy of the recorder based on the pyrotannic acid analysis for CO is given in Table 6.

TABLE 6.—*Accuracy of CO recorder with six couples over a period of six months, based on results of CO analyses by the blood-pyrotannic acid method*

[Concentrations of CO in air ranged up to about 4 parts per 10,000]

Month, 1924	Total number of comparisons	Deviations of recorder (parts CO per 10,000)					
		Positive			Negative		
		Number	Maximum	Average	Number	Maximum	Average
January	7	5	1.2	0.6	2	0.4	0.2
February	18	14	1.5	.5	4	.5	.2
March	31	27	1.5	.6	4	1.1	.6
April	28	22	1.6	.5	6	1.2	.4
May	31	17	1.1	.4	14	0.6	.3
June	29	19	1.3	.5	10	1.1	.4
July	25	20	1.7	.7	5	1.4	.5
General average				0.54			0.37

Most of the discrepancies in Table 6 indicate slightly higher CO as determined by the recorder. Although a few individual determinations showed rather large discrepancies, several causes that are not due to the recorder possibly contributed to these discrepancies. These causes may have been incomplete mixing of gases in the chamber, accidental irregularities in rate of sampling, and errors of analysis. The average deviations, positive and negative, hardly exceed the analytical errors of the blood-pyrotannic acid method. However, the results are especially interesting because they indicate no decrease in sensitivity of the recorder during a period of usage exceeding six months.

Throughout the tests the chemists engaged in the physiological experiments were guided chiefly by the analyses of the recorder.

OPERATION OF RECORDER AT THE LIBERTY TUNNELS

The recorder shown in Plate I (p. 6) has been continuously in use at the Liberty tunnels since August 1, 1924, and on January 1, 1925, it was still operating satisfactorily and without evident change in sensitivity. The record for Wednesday, October 1 (Pl. III), is presented as typical.

The fans run from about 7 o'clock in the morning till nearly midnight. As long as the fans run the gas sample taken by the recorder is truly representative of tunnel conditions. From midnight through the early morning hours the tunnels have natural ventilation. During these hours ventilation may be caused by the wind, by differences in barometric pressure, by temperature differences, or by the traffic in

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the tunnel.[26] On the other hand, on quiet nights at intervals when there is no traffic, mass movements of air may cease entirely. At times of natural ventilation the air in the ventilating shafts, in the air passageways in the fan house above the tunnels, and in the stack vents may move either upward or downward or be motionless. Plate III shows a peak at 1.35 a. m. of about 1.3 parts of CO per 10,000. This is probably due to warm exhaust gas rising in the ventilating shaft and so tending to accumulate some CO in the fan-house airways above. Mass movements of air through the fan house must have ceased. Hence this peak probably does not represent conditions in the tunnel at the time, although it indicates the true concentration of CO in the fan inclosure at the point from which the recorder draws its air sample. After this peak the CO dropped rather abruptly and continued at about 0.1 to 0.3 part per 10,000 until 6.30 a. m. This probably represents actual conditions in the tunnel with a natural ventilating current carrying tunnel air upward through the fan house to the discharge stacks. However, no corroborative observations on the ventilation were made then.

About 6.30 a. m. there was a sharp increase in the CO and the fans were started at 50 r. p. m. about 7 o'clock, and apparently drew out some accumulated CO because the concentration rose to about 1.1 parts per 10,000 and then decreased. At 9.40 the recorder was stopped for the purpose of cleaning and oiling the mechanism and supplying ink and about 3 pounds of fresh sulphuric acid. The attention of a man for 10 to 30 minutes is needed daily for these duties. During most of the day the concentration ranged around 0.5 and occasionally rose to about 1 part per 10,000. Between 4.30 and 6.30 p. m. the traffic peak occurs in the west tunnel, which is used by the traffic outbound from Pittsburgh. The recorder shows a maximum for the day about 1.6 parts per 10,000, and between 5 and 6 p. m. the CO ranged around 1 part per 10,000. Thereafter the concentration was mostly below 1 part, ending with 0.4 part per 10,000 at midnight.

All the records show that the ventilation has been more than ample since 4 parts CO per 10,000 parts of air is a tolerable maximum for one hour's exposure. At no time since the recorder was installed has the CO in this tunnel exceeded 4 parts per 10,000 of air.

OTHER APPLICATIONS OF THE RECORDER

The recorder previously described was tried only with carbon monoxide and with hydrogen in air, but the thermoelectric method of analysis is by no means limited to these gases. Hopcalite or other

[26] Fieldner, A. C., Yant, W. P., and Satler L. L., jr., "Natural ventilation in the Liberty tunnels," Eng. News-Record, vol. 93, Aug. 21, 1924, pp. 290-291.

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catalyzers of oxidation can act on many combustible gases mixed with air or oxygen, either at the temperatures heretofore employed or else at higher temperatures. The heat of oxidation of any combustible gas in considerable dilution in air or oxygen or the reduction of oxygen in a combustible gas can thus be employed as a means of recording the concentrations. Temperatures of the environment about the cell may be increased by surrounding the cell and preheating coils with the saturated vapor of a liquid of higher boiling point than water or by an electrically-heated or flame-heated solid or liquid medium under thermostatic control. At higher cell temperatures binary mixtures of air and methane may be analyzed, or air with any of the hydrocarbon gases or vapors such as gasoline, acetylene, or benzene, and vapors of many other organic compounds such as alcohol, aniline, acetone, ether, formaldehyde, and many more. Even the gaseous compounds of sulphur or phosphorus may be determined by the method if a suitable purifying system and catalyst are employed.

The apparatus may be used to record the progress of some chemical reactions that involve the removal or addition of a gaseous component, provided that carbon monoxide can, without influencing the reaction, be introduced in uniform proportion into the gases prior to the reaction. For instance, the ammonium carbonate leaching process for copper requires oxidizing with air, a cuprous ammonium carbonate in water solution to cupric ammonium carbonate, and for efficient oxidation the air must be supplied in quantity to maintain about 50 per cent excess oxygen under various conditions of volume and concentration.[27] If carbon monoxide is introduced into the air stream in a uniform ratio of about 5 volumes of CO to 10,000 volumes of air, a recorder arranged for highest sensitivity can be made to indicate the oxygen consumption by the increase in concentration of the CO as oxygen decreases. Similar applications may be made in other gas reactions.

SUMMARY AND CONCLUSIONS

The apparatus described has been developed to analyze and record automatically carbon monoxide when present in very low concentrations, especially that in the atmospheres of vehicular tunnels. It is based on the thermoelectric effect produced in differential thermocouples when air containing CO is passed through a catalyst of hopcalite surrounding the hot junctions of the thermocouples. Cells holding hopcalite catalyst with differential couples of 6, 12, 24, 48, and 96 pairs of couples were made. These were placed in a constant-temperature environment, usually saturated steam, and

[27] Benedict, C. H., and Kenny, H. C., "Ammonia leaching of Calumet and Hecla tailings," Trans. Am. Inst. Min. and Met. Eng., vol. 70, 1924, pp. 595-610.

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the couples were connected electrically with a recording potentiometer.

A complete unit CO recorder included a motor-driven blower for the gases, a gas cleaner and purifier of sulphuric acid, caustic soda material, activated charcoal, filters of absorbent cotton, and fused calcium chloride drier, a flow meter arranged to maintain a constant rate of flow of gas through the cell, and copper coils for bringing the gases to the temperature of the cell environment before entering the cell. After passing through the cell the gases were wasted through a guard of fused calcium chloride to prevent entrance of water vapor. The recording potentiometer included mechanism for closing an electric circuit to ring a warning bell or operate signals as long as the CO exceeds a predetermined concentration. Some of the characteristics of the apparatus are as follows:

1. The gas purifier restrained all gases except CO, H_2, CH_4, CO_2, and the components of air except water vapor. Of these gases only CO and H_2 exert an important effect on the recorder under the operating conditions. The conditions can be so arranged that the hydrogen has no material effect upon the accuracy of the CO records.

2. The potentials generated by the cells increase regularly with the numbers of differential thermocouples employed.

3. The potentials first increase rapidly with increasing rates of gas flow, reach a maximum, and then decrease. The maximum potentials for different concentrations all occur at substantially the same rate of gas flow. Operation at this rate gives accuracy, highest sensitivity, and more rapid response to changes in CO concentrations.

4. A cell 5.63 cm. deep gave highest potentials when the hopcalite was 3.38 cm. deep. This hopcalite covered two-thirds of the distance between the hot and cold thermojunctions.

5. A cell refilled several times with fresh hopcalite gave analyses agreeing to ± 10 per cent based on the CO in the gas. It is best to calibrate a cell after each filling by determining the potentials produced by air containing CO in known concentrations. An apparatus of flow meters for diluting with precision CO with air to concentrations of 0.005 to 50 parts per 10,000 (0.5 to 5,000 parts per million) reduced the errors of calibration to 5 per cent or less.

6. Hopcalite gradually deteriorated unless protected by the purifying system mentioned above. With this system no evident deterioration has occurred through a period of five months' continuous use.

7. When 2 per cent water vapor was added to the gases at 100° C. the potentials were reduced 14 per cent. At lower temperatures the poisoning effect of the moisture on the catalyst is augmented.

8. Fifteen per cent of the CO entering a cell at 100° C. escaped unoxidized when the gases passed at the best rate of flow, that is, the

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flow producing maximum potentials. The best rate of flow is thus determined by a balance between the quantity of heat generated and the losses from conduction and from escape of CO unoxidized.

9. At the best rate of flow the cells generate about 66 per cent of their theoretically maximum thermoelectric potentials. With 15 per cent of the potential heat escaping in unoxidized CO, 19 per cent of the heat was seemingly lost through conduction.

10. A recorder with 12 differential couples operating at a flow of 31 liters per minute responded to various changes in CO concentration in 20 seconds. The corresponding change in the record was about 70 per cent completed in 1 minute, 90 per cent in 2 minutes, and 100 per cent in 4 to 8 minutes. The speed of response increases with the rate of flow.

11. Hydrogen alone in air gave no thermoelectric effect when passed through a cell at a temperature of 25° C. With the cell and hydrogen at 100° C. it produced a maximum thermoelectric potential only 15 per cent of the theoretically maximum potential according to calculations based on the heat of reaction of hydrogen and oxygen. This potential was generated at a rate of flow about one-sixth of the best rate for CO. At the best rate for CO the hydrogen exerted only 7 to 8 per cent of its theoretically possible effect. At 127° C. the potential developed by hydrogen increased threefold over that at 100° C. while the best rate remained the same.

12. By operating the recorder cell in an environment of 25° C. and passing through it hydrogen containing traces of CO, a small uniform proportion of air being added as oxidizer, the CO can be accurately determined and recorded.

13. By operating the recorder cell in an environment of 100° C. or higher and passing through it air or oxygen containing small quantities of hydrogen at the best rate of flow for hydrogen, the hydrogen present can be analyzed and recorded. When hydrogen is to be determined, CO should be absent or else eliminated by a preliminary selective oxidation, which has the advantage of permitting determination of both the gases when they are present together.

14. Carbon monoxide in automobile exhaust gas is accompanied by hydrogen in average volume ratio of 1 (of CO) : 0.4 (of H_2). This proportion of hydrogen causes an increase of 3 to 5 per cent in the analyses of CO in vehicular tunnels based on the actual CO present. A recorder operating in a vehicular tunnel thus indicates slightly higher CO than is actually present unless the calibration is modified to allow for the effects of the hydrogen. Since the errors are small, however, and are on the side of safety, it is not essential to heed them.

15. The recorder is adapted to the determination of CO in relatively low concentrations in air. High concentrations may be determined by diluting the gases with a large definite proportion of air,

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say, 1 to 100, before passing them through the recorder and then allowing for the dilution in reading the concentrations.

16. A recorder having a cell of 48 couples has given continuous and satisfactory service at the Liberty tunnels, Pittsburgh, Pa., for five months and was still in service at the end of 1924. It records on a time chart the CO in parts per 10,000 and fractions thereof, being sensitive to about 0.02 per 10,000 (2 parts per million). The range of this apparatus is from none to 9 parts of CO per 10,000 of air. A warning bell is arranged to ring when the CO reaches a concentration of 4 parts per 10,000 or more.

This method of CO analysis is the most accurate and sensitive yet devised for small concentrations of CO in air. A sensitivity of 1 part per million is readily attained.

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